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Real-Time Sensing of Soil Nitrate Concentration in the Parts per Million Range While the Soil Is in Motion

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Reactive nitrogen (Nr) is a term used to describe non-nitrogen gas (non-N₂) forms of nitrogen (N) in the biosphere. It causes major pollution problems when it occurs in excess, and it has many sources, including fertilizers used in production agriculture. Currently there is no on-the-go soil nitrate sensor that could guide the application of the optimal amount of fertilizer, which often varies significantly within a field. We report for the first time nitrate-in-soil measurements performed on moving soil samples at concentration levels relevant for fertilizer application. An infrared emission technique called transient infrared spectroscopy (TIRS) was tested on soil samples spiked with different nitrate concentrations in the parts-per-million range and moving at a velocity of 2.6 m/s (5.8 miles per hour) in the laboratory. The TIRS Fourier transform infrared (FT-IR) spectra were modeled by partial least squares and produced a standard error of cross-validation (SECV) of 6.3 parts per million (ppm) N and an R^2 of 0.938 for 512-scan spectra. These results are compared to those using fewer TIRS scans and to those from photoacoustic spectroscopy (PAS) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements on stationary samples. TIRS 128-, 32-, and 8-scan spectra yielded SECVs of 11.2, 11.4, and 18.4 ppm N and R^2 values of 0.800, 0.831, and 0.583, respectively. The PAS and DRIFTS measurements produced SECVs of 12.4 and 9.0 ppm N and R^2 values of 0.766 and 0.876, respectively.

Index Headings: Soil nitrate; Transient infrared spectroscopy; Photoacoustic spectroscopy; PAS; Diffuse reflectance; DRIFTS.

INTRODUCTION

An overabundance of reactive nitrogen (Nr) in the biosphere puts air, soil, and water resources at risk. Nr has a negative impact on ecosystems, biodiversity, human health, and climate stability to the extent that the environmental problems associated with Nr are now recognized as a central environmental challenge of the twenty-first century.^{1–3}

Agronomists and soil scientists are currently investigating ways to reduce Nr pollution originating from crop production. One approach would be to differentially apply nitrogen fertilizer only on soils where additional nitrogen is needed for optimum crop production, but currently there is no mobile,

real-time sensor that can directly measure soil nitrate concentrations in the field for mapping purposes or for allowing precise application of nitrogen fertilizer. Such a sensor could allow the optimal amount of nitrogen to be applied for crop production while reducing environmental problems, such as ground- and surface-water contamination.

The ideal sensor would make on-the-go (in motion) measurements directly on freshly turned soil without sample preparation, be noncontact, have a parts-per-million nitrate sensitivity, and have a fast enough response time to be compatible with typical farm equipment speeds in the field, which average 2.7–3.6 m/s (6–8 miles per hour [mph]). A mid-infrared spectroscopic technique called transient infrared spectroscopy (TIRS)^{4–5} was tested for compatibility with these requirements.

TIRS is a version of thermal emission spectroscopy, but it avoids the self-absorption problem that often results in production of a blackbody emission spectrum that has no chemical information. In this study, TIRS measurements were made on soil moving past the emission-collection optics of an Fourier transform infrared (FT-IR) spectrometer. Figure 1 shows how TIRS works. A jet of hot air heats the soil surface just as it enters the field of view of the spectrometer. As a result, the emission viewed by the spectrometer comes from a thin, hot surface layer that is too thin for appreciable self-absorption to occur. Although this layer thickens over time by thermal diffusion, the soil motion carries it out of the field of view before it can do so, and the emitting layer viewed by the spectrometer remains thin. The resulting emission spectrum, according to Kirchhoff's Law of Thermal Radiation, has the same information as an absorbance spectrum has. TIRS has been applied on line to several manufactured materials,⁶ and it has been successfully demonstrated on various natural materials, including corn kernels and wood chips.^{7–8}

Our target here is nitrogen in nitrate form rather than total nitrogen because nitrate has direct relevance to soil fertility during the same growing season in which it is applied. In contrast, total nitrogen is predominantly organic nitrogen (mostly amino acids and amino sugars) bound up in the soil organic matter. This organic nitrogen is not immediately available for plant uptake but does gradually become available as the soil organic matter decomposes (nitrogen mineraliza-

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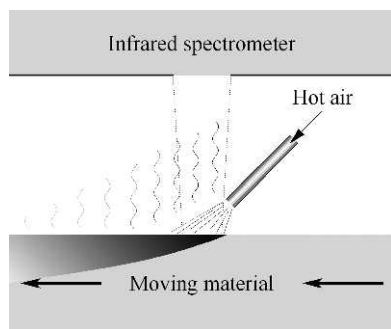


FIG. 1. Schematic of the TIRS analysis process. Hot air striking the moving sample causes a thin surface layer of the sample to radiate a structured spectrum in the infrared, which the spectrometer records. The heated layer moves out of the spectrometer field of view before it can thicken and cool, degrading its spectrum to that of a blackbody.

tion). This long-term, slow release of nitrogen from the organic phase is a major source of soil fertility, but it generally proceeds too slowly to supply all of the nitrogen needed by a growing crop.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) has been used previously to determine nitrate in soil. Ehsani et al.⁹ found that the area under the principal nitrate peak (1390 cm^{-1}) in DRIFTS spectra was proportional to nitrate concentration if the soil was diluted with potassium bromide. They were unable, however, to detect nitrate below 400 parts per million (ppm) in undiluted soil. They were able to quantify the nitrate concentration in neat soils containing 400–3000 ppm nitrate nitrogen by using a continuous wavelet transform both to reduce the noise in the spectra and to remove specular reflection effects. This treatment let them achieve a R^2 of 0.878 and a standard error of calibration of 248 ppm.

Linker's group has extensively studied determining nitrate levels in soil pastes using attenuated total reflectance FT-IR (ATR FT-IR).^{10–13} They found that the most accurate measurements required first determining the type of soil and then applying a calibration specifically for that soil type.^{11,13} They used a combination of principal component analysis and neural networks to identify the soil type and then partial least squares (PLS) to determine the nitrate concentration, resulting in determination errors of 6.2–13.5 mg N/kg soil (dry basis), depending on the soil type.¹³

Choe et al.¹⁴ have also used ATR FT-IR of soil pastes to determine nitrate concentrations. They used second-order derivatives of the spectra to reduce the effect of carbonate features near the 1390 cm^{-1} nitrate peak, which can interfere with the analysis.¹⁰ The root mean square error was 18.6 mg N/kg soil and R^2 was 0.969 for the validation set when agricultural field soil containing 6–8% calcium carbonate and up to about 500 mg nitrate N/kg soil (dry basis) were analyzed with a PLS model. ATR requires good optical contact with the soil, so it is not a viable sampling technique for real-time field analysis.

In some ways, the application of near-infrared (NIR) spectroscopy to soil analysis is more advanced than that of mid-infrared spectroscopy. NIR reflectance spectroscopy has been successfully applied to determining total nitrogen in soil in the laboratory.^{15–17} Stenberg et al.¹⁸ surveyed the application of NIR reflectance to determining total nitrogen and calculated an average R^2 of 0.94 from published studies. NIR has also been used in the field. Kusumo et al.¹⁹ have

demonstrated a fieldable NIR-based reflectance probe for determining total nitrogen from soil cores. They achieved R^2 values of 0.90–0.96 and standard error of cross-validation (SECV) values of 0.02–0.04% for various configurations. Even a tractor-mounted system for on-the-go measurements has been demonstrated.²⁰ Determining nitrate levels using NIR, however, has been less successful. Freschet et al.¹⁵ had some success determining nitrate with NIR reflectance. They achieved $R^2 = 0.81$ and $\text{SECV} = 41\%$ of the mean concentration. On average, however, the results have not been as good. The survey by Stenberg et al.¹⁸ of published studies reporting nitrate determinations using NIR reflectance had an average R^2 of only 0.04.

The studies reported in the literature have generally involved nitrate levels of a few hundred parts per million and higher. All the samples examined here have nitrate-nitrogen levels below 100 ppm. This lower range is more consistent with the fact that critical soil nitrate levels below which crop yields commonly respond to nitrogen fertilization are about 25 mg/kg.^{21–23}

MATERIALS AND METHODS

The samples were created by gathering local surface soils (0–15 cm deep) from a Hayden loam (classified as fine-loamy, mixed, superactive, mesic Glossic Hapludalfs), which is free of carbonate. Carbonate at sufficiently high levels can interfere with infrared-based nitrate determinations.¹⁰ The soil was air dried and then divided into 11 approximately 1 kg samples. A 14 g portion of the air-dried soil was analyzed for moisture content, allowing the calculation of the oven-dried equivalent mass. A 1443.25 ppm solution of potassium nitrate (KNO_3), corresponding to 200 ppm N, was prepared. To produce samples with various levels of nitrogen, 50 mL aliquots made of the KNO_3 solution diluted with an appropriate amount of water were poured onto the samples in zip-lock bags. Each soil sample was then thoroughly mixed by shaking the bag by hand and mixing the soil for approximately 5–10 min. A portion of each sample was sent to a service lab for nitrate testing. The service lab extracted the samples with 2 M potassium chloride (KCl) according to the procedure outlined by Gelderman and Beegle.²⁴ The samples were analyzed on a Lachat Quik-chem KIA 4000+, and the standard deviation of the measurements was 1.85 ppm. The N concentration of the samples ranged from 14 ppm for the sample with water but no KNO_3 added to 93 ppm for the sample with 50 mL undiluted KNO_3 solution added. The spiked samples were kept frozen in sealed plastic bags until they were either analyzed as moist soil or oven dried for analysis as dry soil.

For each TIRS spectrum, a moist soil sample was placed in a track along the outer rim of a 43 cm diameter platter, which was spun to mimic the motion of soil passing by an analyzer mounted on a fertilizer applicator. A Bomem MB100 FT-IR spectrometer was fitted with a side port and an external 9 cm focal-length mirror to focus the field of view of the spectrometer down onto the stream of soil moving past on the platter. The spectrometer viewed a 4 mm wide swath of the soil stream centered 19 cm from the center of the platter. The platter spun at 130 revolutions per minute (rpm), giving the soil a linear speed of 2.6 m/s (5.8 mph) through the spectrometer field of view. A jet of hot air was applied to the soil by an air heater (Leister 3000 hot air tool) within the spectrometer field of view to produce the thin, heated layer that TIRS requires. The hot-air tool ran at 460 W with an air flow of 0.5 L/s. Its

nozzle was 15 mm wide and 3 mm tall and was positioned within 1 cm of the soil stream. In the field, soil would pass the analyzer only once. In this laboratory arrangement, the soil spins repeatedly past the spectrometer. To prevent the bulk of the sample from being warmed by the repeated passes through the hot-air jet, a jet of helium that had been cooled by passage through a liquid nitrogen bath was aimed onto the soil just downstream from the spectrometer field of view. In this way, the soil was always near room temperature as it entered the hot jet and the spectrometer field of view. Despite the cooling jet, the hot-air jet did slowly dry out the soil during the analysis. TIRS spectra consisting of 8-, 32-, 128-, and 512-scans were gathered, in that order, from each sample, so the soils were driest for the 512-scan spectra. Samples were analyzed in random order to prevent any instrumental drift from influencing the chemometric results. The FT-IR spectrometer was fitted with a wide band liquid nitrogen-cooled mercury cadmium telluride (MCT) detector, and its normal infrared source was replaced by a liquid nitrogen-cooled cold source. The spectrometer scanned at 1.50 cm/s optical-path-difference velocity and 8 cm⁻¹ resolution, taking approximately 0.8 s for each scan. The spectra were acquired in from 7 min (for 512 scans) to 7 s (for 8 scans). The raw, single-beam spectra were not normalized but were used directly in the PLS analysis. Normalization does not increase the accuracy of the analysis, so a real-time field analysis would not include this additional step.

For the DRIFTS and photoacoustic spectroscopy (PAS) spectra, three samplings were taken from the moist soil sample at each nitrogen level and placed in 6 mm diameter (45 mm³ volume) aluminum cups. DRIFTS spectra of the moist samples were acquired, and then the samples were dried overnight in an oven at 100 °C. The dried samples were then stored in a desiccating cabinet until they were analyzed by both DRIFTS and PAS. DRIFTS spectra were acquired using a Harrick Praying Mantis DRIFTS accessory mounted in a Nicolet Avatar FT-IR spectrometer. Spectra were taken with 8 cm⁻¹ resolution at a 0.1581 cm/s scanning speed, and 512 scans were co-added. The raw spectra were converted using the Kubelka-Munk Function and a powdered potassium bromide reference. The FT-IR PAS spectra were taken using a MTEC PAC300 photoacoustic detector mounted in a Digilab FTS 7000 FT-IR spectrometer. The detector was purged with helium immediately prior to spectrum acquisition. A small amount of magnesium perchlorate desiccant was placed beneath the sample to eliminate any water vapor in the detector's sample chamber. Spectra were taken with 8 cm⁻¹ resolution at a 2.5 kHz scanning speed, with the co-addition of 512 scans. Spectra were normalized relative to the spectrum of a carbon-black-coated membrane.

PLS was performed using the PLSplus/IQ module of GRAMS/AI, Version 7 (Thermo Galactic). A separate, optimum PLS model was determined for each set of spectra studied. The very different signal acquisition modes of TIRS, PAS, and DRIFTS and the resulting differences in spectral properties (e.g., signal-to-noise ratio [S/N], peak overlap, and peak strength) result in optimum PLS models involving different spectral preprocessing and different spectral ranges. The TIRS data sets involving different numbers of scans acquired for each spectrum were, of course, much more similar to one another, but the optimum models for those data sets still differed modestly from one another both because the S/Ns of

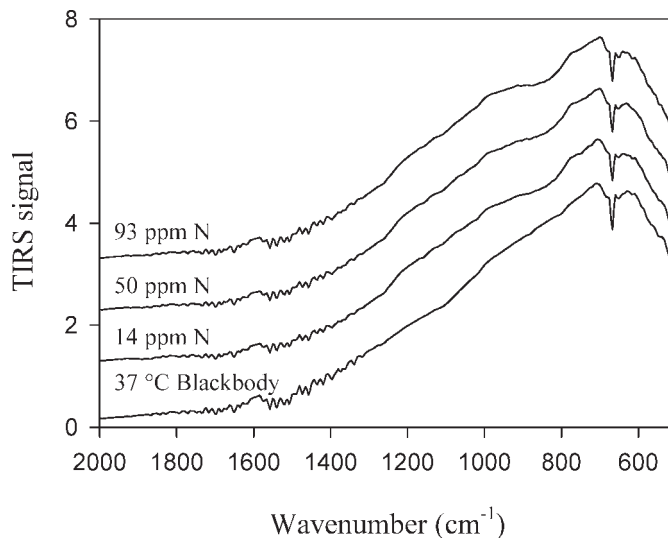


FIG. 2. Three single-beam, 512-scan TIRS spectra of soil containing various levels of nitrate are compared to a 37 °C blackbody spectrum. Soil samples were moving at 2.6 m/s during spectrum acquisition.

the spectra depend on the number of scans and because, as previously noted, the soil grew drier as the 8-, 32-, 128-, and 256-scan spectra were acquired, in that order, altering both the spectral and thermal properties of the soils. The number of factors used in each PLS model was determined by using single-elimination cross-validation and calculating the prediction residual error sum of squares (PRESS). In a plot of PRESS versus the number of PLS factors, PRESS reaches a minimum at the optimum number of factors.²⁵

RESULTS AND DISCUSSION

Figure 2 shows single-beam TIRS spectra of soils at three different nitrate levels. A 37 °C blackbody spectrum is included for comparison. It is apparent that the TIRS spectra consist mostly of a near room-temperature blackbody spectrum with smaller, TIRS-induced emission features added. The differences

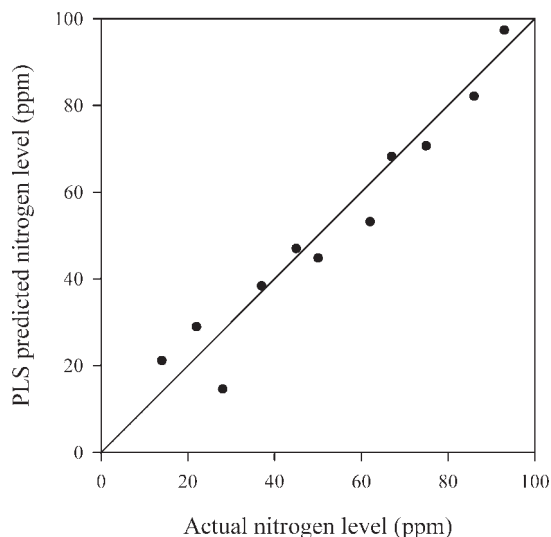


FIG. 3. Cross-validation for the PLS model of 512-scan TIRS spectra of soils with various levels of nitrate. SECV = 6.3 ppm N and $R^2 = 0.938$.

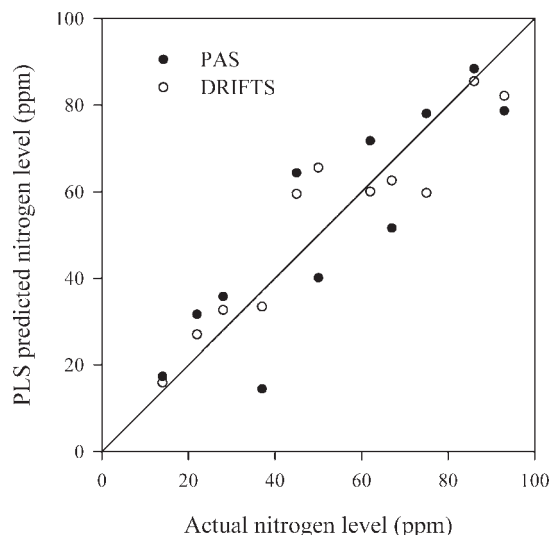


FIG. 4. Cross-validations for the PLS models of PAS and DRIFTS spectra of dry soils with various levels of nitrate. For the PAS model, SECV = 12.4 ppm N and $R^2 = 0.766$. For the DRIFTS model, SECV = 9.0 ppm N and $R^2 = 0.876$.

among the TIRS spectra related to nitrate level are subtle. The main nitrate emission band is broad and appears in the range 1390–1350 cm^{-1} .^{10,12,26} In part because of its breadth, the peak is largely hidden from casual inspection of the spectra by the water-vapor absorption lines in that region. PLS modeling, however, correlates the spectra with the nitrate level quite well. Figure 3 shows the single-elimination cross-validation plot for 512-scan TIRS spectra of 11 soil samples. The PLS model used the 1219–1501 cm^{-1} range of the single-beam spectra, which were preprocessed using variance scaling and multiplicative scatter correction (MSC)²⁷ and were converted to second derivatives (19-point Savitzky–Golay smoothing) prior to the modeling. The PLS model used four factors. SECV is 6.3 ppm N and R^2 is 0.938. The 512-scan spectra required slightly under 7 min to acquire, so spectral acquisitions of that length would provide only modest spatial resolution if used on a farm implement moving at 2.6 m/s, the speed of the samples during the TIRS acquisition. Fortunately, the statistics degrade only slowly as the number of scans acquired is reduced. Similar PLS models based on 128-, 32-, and 8-scan spectra of the same samples yielded single-elimination cross-validations with SECVs of 11.2, 11.4, and 18.4 ppm N and R^2 values of 0.800, 0.831, and 0.583, respectively. Preprocessing was optimized separately for each of these models. The 128-scan model used mean centering, MSC, and 19-point second derivatives; analyzed the 1219–1450 cm^{-1} range; and required four factors. The 32-scan model used variance scaling and MSC, analyzed the 1219–1501 cm^{-1} range, and required two factors. The 8-scan model used variance scaling, MSC, and 19-point second derivatives; analyzed the 1200–2199 cm^{-1} range; and required three factors.

For comparison with these results, we also examined the soils by both PAS and DRIFTS. Three soil samples at each nitrate level were oven dried, and then 512-scan spectra were acquired using both of these techniques. The three spectra at each nitrate level were then averaged together, and the resulting 11 spectrum data sets were modeled using PLS. Figure 4 shows the single-elimination cross-validation plots for the best models. The PAS and DRIFTS models have SECVs of 12.4

ppm N and 9.0 ppm N and R^2 values of 0.766 and 0.876, respectively. The PAS model used variance scaling, MSC, and 15-point second derivatives; analyzed the 1231–1539 cm^{-1} range; and required five factors. The DRIFTS model used variance scaling, MSC, and 21-point second derivatives; analyzed the 1250–1828 cm^{-1} range; and required five factors. The same samples were also analyzed by DRIFTS while still moist (i.e., before oven drying). The best PLS model for those 11 averaged spectra has a SECV of 14.3 ppm N and R^2 of 0.679. The model used variance scaling and MSC, modeled the 1200–1751 cm^{-1} range, and required four factors. These results are somewhat worse than the 6.3 ppm SECV for the 512-scan TIRS spectra model, but because of the sample motion during the TIRS measurement, it encompasses roughly 50 times as much soil as do the three PAS and DRIFTS measurements at each nitrate level combined. This sample averaging contributes to the superior TIRS result.

CONCLUSION

The results reported here show that TIRS is a promising noncontact approach for quantitatively measuring nitrate levels in soil while the soil is moving past the analyzer at speeds typical of fertilizer applicators and other farm equipment. Several changes could be made to reduce the data acquisition time and hence the distance over which an in-the-field measurement would be made. These include reducing the spectral resolution or using a faster, nonscanning spectrometer, such as a filter-based unit, a dispersive focal-plane-array instrument,²⁸ or a stationary FT-IR spectrometer.²⁹ The thermal excitation of the soil and the light collection optics could also be optimized for this particular application. TIRS is not limited to nitrate levels. Any soil property having a spectral signature in the fingerprint region of the mid-infrared spectrum of soil should be accessible to TIRS analysis.

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